1857

DIALDEHYDE STARCH AS A PRETANNING AGENT FOR VEGETABLE-TANNED SOLE LEATHER*

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ABSTRACT

A pilot plant evaluation of dialdehyde starch as a pretanning agent for the tanning of sole leather is described. Effects of variables were tested, using packs of 10 hides each. The results from 30 test packs were used to arrive at the optimum conditions. This final process was confirmed by processing 10 consecutive packs in which the dialdehyde starch and vegetable tannin liquors were reused with appropriate strengthening. The proposed process permits a substantial reduction in processing time, and the cost data developed indicates that the process can be expected to be competitive with existing industry costs. The process should be easily applicable to existing sole leather tanneries.

INTRODUCTION

Recent years have witnessed an increase in leather substitutes from the plastic industry. More than 70% of the sole leather market has been lost. The tanning of sole leather with vegetable tanning materials is still a rela-

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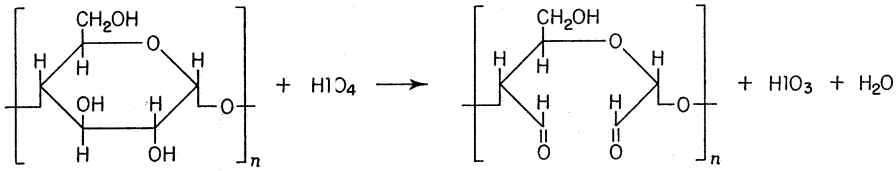
tively long process in spite of some chemical and mechanical improvements. A rapid and economical sole leather process would be an advantage.

Investigations have shown that dialdehyde starch has tanning action (1–4). A rapid process was developed in the laboratory for pretanning heavy hides with dialdehyde starch and retanning with vegetable extracts to produce sole leather (5). The leather produced had the chemical and physical characteristics of sole leather and was comparable to current commercial leather. The economic feasibility of this process depends upon its adaptability to existing tannery equipment and upon balancing the cost of the replacement material against the time saved and the reduction in the amount of vegetable tannins required. To determine these points a pilot plant–scale tannery test was conducted. These tests and results are the subject of this paper.

Dialdehyde starch is a polyfunctional aldehyde derived from starch by periodate oxidation. The glucose units of the starch molecule are oxidized to a dialdehyde structure by periodic acid as follows:



starch *dialdehyde starch*

Although this reaction was known for some time (6), it was of little interest outside the laboratory until a convenient and inexpensive production method was developed for regenerating the periodic acid (7–10). Further process improvements were found which made dialdehyde starch potentially available at low cost from corn starch (11).

THE SCOPE OF THE PILOT PLANT TESTING

The equipment utilized in carrying out this investigation at the Armour Leather Company Sole Leather Tannery in Williamsport, Pa., included 2 paddles, one tanning drum (8′ x 4′), a series of rocker vats sized to handle 10 whole hides, 7 mixing tanks for the preparation of liquors, a centrifugal pump for moving the tan liquors, and numerous miscellaneous items. The beamhouse, scrubhouse, and finishing facilities of the Armour tannery were also used.

The proposed process, based on laboratory-scale testing at Eastern Regional Research Laboratory (11), served as a starting point for this work. This proposed process consisted of five basic steps, namely, (*a*) deliming and bating the unhaired and fleshed hides, (*b*) water-washing delimed stock to remove ammonium salts, (*c*) pretanning with dialdehyde starch, (*d*) water-washing

the pretanned hides, and (*e*) vegetable retanning, starting in strong tan liquors.

The proposed formula for the dialdehyde starch liquor was as follows:

8% sodium sulfate based on the total liquor volume

5% dialdehyde starch based on the white hide weight

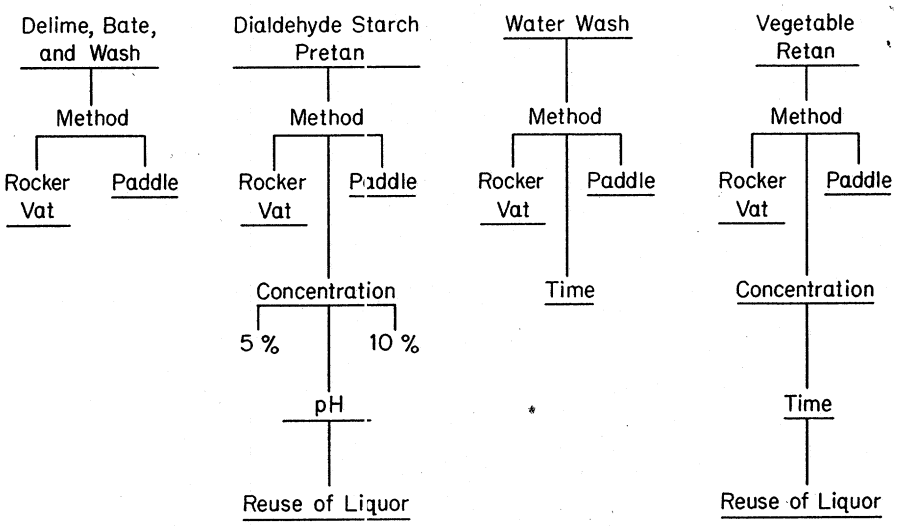
6.3% sodium bicarbonate based on the white hide weight.

Adjusted to pH 8.0

The variables, process and equipment, in each of these steps subjected to study are shown schematically in Table I. The conventional sole leather

TABLE I

SCHEMATIC OUTLINE OF VARIABLES SUBJECT TO STUDY UNDER TERMS OF THE CONTRACT



beamhouse operation for preparing the hides to be unhaired and fleshed was carried out in the Armour tannery. The operations following the tannage in the pilot plant which are normal to sole leather production, namely, wheel extracting, tempering, bleaching, wringing, oil wheel loading, setting out, drying, and finishing, were also carried out in the Armour tannery. In the final 10 tests the wheel extracting and tempering were done in the pilot plant to check material consumption.

In order to evaluate the various aspects of the process under study it was necessary to accumulate as much "in-process" analytical data as possible. Therefore, on each of the proposed tests it was decided to analyze samples of the white hide before and after bating, samples of the new and sap bate waters,

samples of the new and sap dialdehyde starch pretan and rinse liquors, and samples of the vegetable tan liquors and/or vegetable extracts used. The shrinkage temperature test on the dialdehyde starch–pretanned stock was used as a measurement of tannage. It was also recognized that visual observations of the stock during process would be of considerable value.

Each pack of finished leather was sampled and subjected to chemical and physical testing to establish its relationship with conventional sole leather. These analyses were carried out according to the Methods of the American Leather Chemists Association and the Federal Specification Method KK-L-311a. The physical tests conducted were compressibility, water absorption, pipiness, and crackiness.

Inasmuch as these studies were directed toward obtaining a leather comparable to conventionally tanned sole leather, it was recognized that some system of rating the leather characteristics would be needed. A Quality Index evaluation was therefore established. Five characteristics of leather which were felt to be affected by the process under study were selected. These were color, undertone, finish, temper, and drawn grain. These are, of course, subjective tests, but it was felt that if an inspection could be carried out systematically it would be helpful in comparing test lots. Each finished back was examined for these characteristics and then given a grade of 5 when considered satisfactory. Lower grades down to 0 were recorded for those backs showing less satisfactory quality for the respective characteristic. Therefore, with 20 backs in each test lot, a score of 100 for any one characteristic would indicate it to be comparable to conventional sole leather. The Quality Index of the lot of leather under examination was expressed as the average of the five rated characteristics, thus the nearer this figure would approach 100, the more satisfactory the leather.

THE EXPLORATORY TESTING

A series of 30 tests, utilizing 10 whole hides each, were conducted to evaluate systematically the procedure and equipment variables outlined in Table I. It is interesting to note that the first test carried out in the pilot plant following in detail the procedure developed at Eastern Regional Research Laboratory produced leather judged to be comparable in all respects with conventional sole leather.

From the results of these 30 tests it was established that:

a. Satisfactory deliming could be obtained in a paddle operation using boric acid rather than ammonium salts. This eliminated the washing step required to remove the excess ammonium salts.

b. The dialdehyde starch pretanning was more a function of time than agitation, and best results were obtained when carried out in the rockers for

a 48-hour period. A "drawn grain" condition resulted when the paddle or drum was used. Using 5% dialdehyde starch on the hide weight, 48 hours were required to obtain complete penetration of the dialdehyde starch in the rockers at pH 8.0, and no advantage was gained when 10% dialdehyde starch was used.

c. The use of 2.8% borax on the weight of the dialdehyde starch facilitated the preparation of the dialdehyde starch pretan liquor. This eliminated the sodium bicarbonate used initially. A 25% dialdehyde starch stock liquor was found to be stable, and the dialdehyde starch liquor could be reused with fortification and pH adjustment with sodium carbonate.

d. Water rinsing the pretanned stock in the rocker for two hours proved satisfactory and eliminated additional handling.

e. The dialdehyde starch–pretanned stock could be vegetable-retanned starting with liquors containing approximately 15% tannin at pH 4 to 4.5 made from a standard sole leather blend of extracts. Three to four days in such liquors in a rocker, followed by wheel extracting and tempering (5 days) gave complete penetration of the vegetable retan. Vegetable retannage as a drum operation resulted in leather with a drawn grain. The wheel extracting and tempering were unnecessary for the belly stock.

f. In one test several bends, bellies, and shoulders were retanned in a drum using a lignosulfonate and a syntan (Orotan). The resulting leather was rather dark in color but did have an extremely smooth grain and was very pliable. Its suitability for sole leather is doubtful, but it could have interest in other fields. The rate of retannage was very rapid, and a drop in the shrinkage temperature was noted.

THE CONFIRMATORY TESTING

Based on the experience gained from the first 30 tests, a tanning procedure was adopted for the final 10 tests which incorporated the operational and process details which had given the best results and appeared to offer the most economic approach.

The following is a detailed description of the process as it was carried out on the final 10 tests (Nos. 31 to 40). These final 10 tests were set up so that they could be put into process consecutively on alternate working days over a period of 3½ weeks.

Hides.—Cowhides were used in all these tests and processed into backs and bellies, except No. 33 where steers were used and processed as bends, double rough shoulders, and bellies.

Ten unhaired, fleshed, and trimmed hides were weighed and transferred from the Armour tannery to the pilot plant as whole hides for each test.

They were then split into sides for further processing except in test No. 33 where the splitting was deferred until after the stock came out of the vegetable retannage. In tests 32 and 37, 20 hides were obtained from the Armour tannery beamhouse. These were split into sides and separated into alternate "lefts" and "rights" so as to make two lots of 20 sides each. One lot was processed through the dialdehyde starch process, and the other was returned to the Armour tannery and processed through their regular rocker tanning operation. In this way two tests were set up to compare the dialdehyde starch process directly with the existing vegetable-tanning rocker process as carried out in the Armour tannery.

Bate and delime.—This was a paddle operation using 2.5% boric acid and 0.1% Oropon N, based on the white hide weight for one hour at 80°F. The ratio of white hide to solution volume was approximately 1 to 5. This bate liquor was not reused. However, on a production-scale basis it could undoubtedly be used two or three times with suitable fortifications.

Dialdehyde starch pretan.—The bated and partially delimed hides were then hung in a rocker vat in which they remained for the dialdehyde starch pretannage, water rinse, vegetable retannage, and final rinse. The ratio of hide to liquor volume was approximately 1 to 5.

The dialdehyde starch liquor was made up to contain 5% dialdehyde starch on the white hide weight and 8% sodium sulfate by volume and was adjusted to pH 8.0 with sodium carbonate. The initial temperature was 80°F. The time in the dialdehyde starch liquor was two days except in tests 33, 36, and 39, where the time was extended to three days because of week-end operations.

The same dialdehyde starch liquor was used for all 10 tests. After the first test it was strengthened with 3% dialdehyde starch on the white hide weight basis, and the sodium sulfate taken up by the hide was replaced.

The dialdehyde starch liquor was prepared from a 25% dialdehyde starch stock liquor which had been prepared at the outset of the final 10 tests. In making up the stock solution, the amount of dialdehyde starch which would be required for the 10 tests was estimated and made up using 2.8% borax on the weight of the actual dialdehyde starch used. This gave a solution with a pH of approximately 5.0 and proved to be stable. The amount of dialdehyde starch per gallon of stock liquor was calculated and served as the basis for measuring the amount of material required for each test. The sodium sulfate content of the liquor was maintained at approximately 8% by volume by means of specific gravity control. That is, it was found that the barkometer reading (1° barkometer equals 1.001 specific gravity) on the initial dialdehyde starch liquor made up was 72°. Therefore, by knowing the actual amount of sodium sulfate used it was possible to calculate the pounds of sodium sulfate per 1° barkometer. Then by measuring the barkometer of the

sap dialdehyde starch liquor from each test (this was found to be approximately 66°). it was possible to calculate the amount of sodium sulfate to add to the next liquor to bring it back to the same sodium sulfate content as the previous test.

Water rinse.—The dialdehyde starch liquor from each test was pumped to the mixer for strengthening and adjustment. Water at 80° to 85°F. was then pumped into the rocker vat, and the stock was rinsed for two hours, after which the rinse water was run to the sewer.

Vegetable retan.—The vegetable liquor used for retannage was made up to contain approximately 15% tannin, from a blend of extracts composed of quebracho, wattle, chestnut, and cutch. The pH of the initial liquor was approximately 4.0. This liquor was pumped into the rocker vat containing the dialdehyde starch–pretanned and rinsed stock at a temperature of approximately 85°F. On the second day it was pumped back to the mixer and strengthened to bring the tannin content to approximately 15%, and the temperature was adjusted to 95°F. On the third day the liquor was circulated through the mixer, and the temperature was raised to 100°F. without any strengthening. No adjustment of the liquor was made on the fourth day. The stock was ready for rinsing and hoisting on the fifth day. On the basis of the schedule followed for these tests, the tanning time was five days in each test except Nos. 33, 36, and 39, where it was four days. This one-day difference in tanning time was due to week-end operations.

Rinse.—The vegetable-retanned stock was rinsed in the same rocker vat in which it was tanned by pumping on water or used rinse liquor at a temperature of 90°F. The stock was rocked for 30 minutes, and the rinse liquor was pumped off.

Cropping.—The sides of leather were hoisted from the rocker rinse and cropped into backs and bellies. In test No. 33, where steerhides were used, the whole hides were cropped into double shoulders, bellies, and single bends.

Finishing bellies.—The tannage of the bellies was completed at this point, and they were therefore transferred to Armour tannery for bleaching, wringing, oil wheel loading, drying, and finishing. In the finishing operations the dried bellies were dipped in water, sammied overnight, sponged, rolled once, and hung to dry.

Wheel extracting (backs and bends).—This operation was carried out in the pilot plant drum, using 12% of a wheel extract based on 70% of the original white weight of the 10 whole hides. The extract, bisulfited quebracho, was introduced into the drum at 120°F., and the drumming time was one hour.

Tempering (backs and bends).—The extracted stock from the drum was laid into vats containing a typical tempering liquor, which had been obtained

from the Armour tannery, at a temperature of 100°F. The time in the tempering liquor was 5 working days (7 calendar days). These tempering liquors were reused for the 10 test lots of leather, as this is conventional practice.

Rinse (backs and bends).—The stock was hoisted from the tempering liquor vat and laid into another vat containing approximately a 12° barkometer liquor and left overnight. The temperature of the rinse liquor was 100°F.

Finishing (backs and bends.)—From the rinse liquor the stock was transferred to the Armour tannery for bleaching, oil wheel loading, setting out, drying, and finishing. The finishing operation consisted of dipping the rough-dried leather into a sour dip, sammying overnight, sponging, wet rolling twice, drying, a polish dip, drying, brushing, and finally a dry rolling.

Finished leather.—The backs and bellies from each test lot were weighed, and the finished weights were recorded. The backs and bends were subjected to Quality Index inspection. The backs from the matched sides, tests 32 and 37, were measured for thickness for comparison with the regular leather from the same packs, and they were examined visually.

Sampling.—The sampling was carried out at the pertinent in-process points to establish as much analytical data as possible on the process and to obtain the data necessary to calculate the tanning costs. The finished leathers from test lots 31, 32, 37, and 40 were sampled for chemical and physical tests.

RESULTS AND DISCUSSION

The pertinent operational data established on the dialdehyde starch pretanning of these 10 test lots have been condensed and are shown in Table II.

TABLE II

DAS PRETAN OPERATIONAL DATA

Tests No. 31 to 40, Inclusive

Test No.	White Weight lb.	DAS %	DAS Added lb.	Scd. Sulfate Added lb.	°Bk. New	°Bk. Sap	pH 2 Day Sap	Shrinkage Temperature °C. 24 Hr.	48 Hr.
31	600	5	30	274	71½	63	7.1	72	78
32	585	3	18	33	71½	64½	7.2	74	78
33	674	3	20¼	27	72	63½	7.5	73	81*
34	560	3	17	26	71½	64½	7.5	72	82
35	600	3	18	26¼	71½	64	7.4	74	82
36	610	3	18¼	26½	72	64½	7.2	76	84*
37	585	3	18	26¼	72	65	7.3	74	82
38	600	3	18	26½	72	65½	7.4	75	81
39	650	3	19½	26¾	72	65	7.1	76	84*
40	590	3	18	24	72	67	7.2	76	82
Total	6054		195	517					

*66 hours
Liquor volume = 400 gal.
pH of new DAS liquor = 8.0
Temperature of DAS liquor, new = 82° ± 2°F.; Sap = 70° ± 2°F.

TABLE III

VEGETABLE RETAN OPERATIONAL DATA

Tests No. 31 to 40, Inclusive

Test No.		1st Rocker Liquor			2nd Rocker Liquor			3rd Rocker Liquor			*Whee Extract lb.	*Tempering Liquor		
		°Bk.	pH	°F.	°Bk.	pH	°F.	°Bk.	pH	°F.		°Bk.	pH	°F.
31	New	83	4.30	83	95	3.95	93	90	3.90	100	50	42	4.00	93
	Sap	74	4.48	76	89	4.12	78	87	4.15	74		43	4.10	66
32	New	84	4.33	85	95	3.95	94	85	4.23	101	50	41	4.00	92
	Sap	75	4.50	80	87	4.23	74	84	4.22	79		43	4.20	66
33	New	86	4.18	82	95	3.95	94	91	4.15	102	57	42	3.98	93
	Sap	77	4.42	76	90	4.05	82	85	4.20	77		45	4.22	66
34	New	83	4.28	83	94	3.95	95	90	4.02	101	48	41	3.95	94
	Sap	76	4.40	78	90	4.02	83	86	4.12	70		43	4.15	68
35	New	85	4.20	83	94	3.95	94	89	4.05	103	51	41	4.02	95
	Sap	77	4.35	78	88	4.20	73	84	4.20	76		41	4.30	68
36	New	87	4.20	82	95	3.98	93	90	4.15	102	52	41	4.15	92
	Sap	78	4.40	76	90	4.20	79	85	4.15	74		41	4.35	67
37	New	85	4.15	82	95	3.98	95	89	4.12	102	50	41	4.05	96
	Sap	78	4.38	77	89	4.20	81	86	4.15	71		42	4.30	68
38	New	87	4.18	83	94	3.98	96	87	4.15	102	51	41	4.30	94
	Sap	78	4.40	79	87	4.22	75	86	4.20	76		42	4.40	67
39	New	87	4.22	84	94	3.95	94	89	4.15	100	55	40	4.15	95
	Sap	78	4.40	78	89	4.15	81	84	4.25	74		40	4.30	67
40	New	85	4.28	85	93	4.05	94	89	4.18	102	50	40	4.10	94
	Sap	77	4.42	78	89	4.15	80	85	4.30	71		41	4.20	68

*Backs or bends only.
Rocker liquor volume = 390 gal.
Tempering liquor volume = 210 gal.

In Table III the pertinent operational data are shown for the vegetable retanning operations. These data are included to serve as the basis for establishing operational controls for the process.

TABLE IV

SUMMARY OF DIALDEHYDE STARCH LIQUOR ANALYSES

Showing Grams DAS per Gallon of Pretan Liquor, Grams DAS Uptake per Pound of White Hide, and Shrinkage Temperatures

Test No.	Grams DAS/Gal.			White Weight lb.	DAS Uptake			
					24 Hours		48 Hours	
	New	Pretan Liquor Sap 24 Hr.	Sap 48 Hr.		Grams per Lb. Hide	Shrink Temp. °C.	Grams per Lb. Hide	Shrink Temp. °C.
31	24.15	14.72	13.02	600	6.3	72	7.4	78
32	29.00	18.93	17.03	585	6.9	74	8.1	78
33	32.14	21.16	16.88*	674	6.5	73	9.1*	81
34	31.68	21.54	19.27	560	7.2	72	8.9	82
35	33.46	26.16	20.29	600	4.9	74	8.8	82
36	35.92	26.04	21.16*	610	6.5	76	9.7*	84
37	36.76	24.60	21.99	585	8.4	74	10.1	82
38	38.27	27.67	22.94	600	7.1	75	10.2	81
39	38.19	28.39	24.45*	650	6.0	76	8.5*	84
40	39.71	29.75	27.78	590	6.8	76	8.1	82
Average				605	6.7	74	8.9	81

*After 66 hours

The in-process and finished leather analytical data developed on these final ten tests are recorded as follows:

Table IV is a summary of the dialdehyde starch liquor analyses which were conducted by the Eastern Regional Research Laboratory. The results are calculated to show the concentration of the dialdehyde starch liquor and the grams of dialdehyde starch uptake per pound of white hide at the end of 24 and 48 hours of pretanning as well as the shrinkage temperatures obtained. These results substantiate the two-day dialdehyde starch pretanning and the practicability of reusing the dialdehyde starch liquor at least 10 times. In fact the build-up of the dialdehyde starch concentration in the liquor when using 3% for strengthening suggests that it would be feasible to use even lower amounts for strengthening.

Table V shows the liquor analyses from tests 31 and 40 only, for the rocker liquors and the tempering liquor. It should be noted that the purity of the rocker liquor held up very well, indicating that no appreciable build-up of nontans had taken place.

TABLE V

SUMMARY OF TAN LIQUOR ANALYSES

Test No.	Liquor	°Bk.	Total Solids	Soluble Solids	Ins.	Non-Tannin	Tannin	Purity	pH
				First Rocker Liquor					
31	New	83	19.20	19.00	.20	5.12	13.88	73.1	4.29
	Sap	74	16.90	16.60	.30	4.85	11.75	70.8	4.48
40	New	85	19.75	19.40	.35	5.67	13.73	70.8	4.25
	Sap	77	17.60	17.35	.25	5.45	11.90	68.6	4.38
				Second Rocker Liquor					
31	New	95	22.40	22.05	.35	5.78	16.27	73.8	3.90
	Sap	89	20.75	20.40	.35	5.72	14.68	72.0	4.02
40	New	93	21.90	21.55	.35	5.94	15.61	72.4	4.18
	Sap	89	20.90	20.25	.65	6.16	14.09	69.6	4.20
				Third Rocker Liquor					
31	New	90	21.25	20.70	.55	5.72	14.98	72.4	3.92
	Sap	87	20.25	19.90	.35	5.50	14.40	72.4	4.00
40	New	89	20.75	20.30	.45	6.16	14.14	69.7	4.15
	Sap	85	20.00	19.45	.55	6.16	13.29	68.3	4.20
				Tempering Liquor					
31	New	42	10.40	10.20	.20	2.18	8.02	78.6	3.90
	Sap	43	10.60	10.60	.00	2.29	8.31	78.4	4.12
40	New	40	9.83	9.60	.23	2.69	6.91	72.0	4.15
	Sap	41	10.10	9.77	.33	2.72	7.05	72.2	4.20

The results of the chemical analyses carred out on the finished backs and bellies are shown in Table VI. Also included are the analytical results obtained on the backs and bellies tanned out in the Armour tannery as controls—tests 32 and 37. These results are considered to be quite comparable with average conventionally tanned leather.

The results of the physical testing carried out on the same test lots of finished leather as used for the chemical analyses are summarized in Table VII. The results of water absorption, pipiness, and crackiness are comparable to those obtained on conventional sole leather.

The quality of the leather produced by this process was carefully evaluated, and the results of the Quality Index ratings of the backs produced during this 10-test run are shown in Table VIII along with the yield of leather based on white weight. This evaluation along with the over-all observations of all the leather produced during the pilot plant study of this process justifies

TABLE VI

SUMMARY OF LEATHER CHEMICAL ANALYSES

Samples from Selected Tests in Final Run

(Results on Dry Basis)

Test No.	Moist	Oil	Ash	Ins. Ash	Salts	Sugar	Hide	Load	Water Sol.	Non-Tan.	Tan.	Comb. Tan.	Deg. Tan.	PH
							Backs							
31	9.3	5.0	9.4	0.1	11.9	9.0	33.1	66.9	36.3	27.0	9.3	25.5	76.9	3.00
32	10.1	3.4	8.5	0.1	10.0	9.5	36.6	63.4	33.6	24.4	9.2	26.4	72.2	3.00
32DN*	10.2	4.0	7.8	0.1	11.1	11.1	36.9	63.1	34.9	24.8	10.1	24.2	65.5	3.10
37	10.3	5.0	7.3	0.1	11.3	11.1	36.0	64.0	33.8	24.5	9.3	25.1	69.8	3.00
37DN*	9.1	6.1	8.7	0.02	13.2	10.6	33.5	66.5	38.0	27.9	10.1	22.3	66.5	2.95
40	8.5	4.3	7.7	0.1	11.6	10.2	36.2	63.8	36.9	25.1	11.8	22.5	62.0	3.42
							Bellies							
31	9.8	4.2	6.1	0.1	6.8	9.6	36.6	63.4	31.2	21.7	9.5	27.9	76.3	2.99
32	10.4	3.9	7.4	0.1	8.0	10.6	36.8	63.2	32.3	23.6	8.7	26.9	73.1	3.05
32DN*	10.2	3.8	7.2	0.1	8.8	10.1	38.5	61.5	33.0	22.9	10.1	24.6	64.0	3.05
37	9.5	5.1	5.9	0.1	6.7	10.3	36.2	63.8	32.5	22.0	10.5	26.1	72.1	3.10
37DN*	8.4	5.3	5.0	0.1	8.1	9.3	38.0	62.0	30.5	20.2	10.3	26.2	68.8	2.95
40	9.3	4.3	6.0	0.1	7.8	9.0	37.8	62.2	31.0	21.6	9.4	26.9	71.2	3.08

*Cross-matched sides processed through Armour tannery for comparison

TABLE VII

SUMMARY OF LEATHER PHYSICAL TESTING*

Samples from Selected Tests (Backs Only) in Final Run

(Results Average of 5 Determinations)

Test No.	Water Absorption ½ Hr.	Water Absorption 24 Hr.	Compressibility (3000#/sq. in.)	Pipiness (3" Mandrel)	Crackiness (3" Mandrel)
31	24.4%	33.0%	3.9%	Do not pipe	Do not crack
32	20.3	32.6	4.3	" " "	" " "
32DN†	24.9	36.7	4.8	" " "	" " "
37	24.7	36.5	3.9	" " "	" " "
37DN†	29.0	37.9	6.4	" " "	" " "
40	26.9	35.9	5.7	" " "	" " "

*Testing according to Federal Specification KK-L-311a
†Cross-matched sides processed through Armour tannery for comparison

TABLE VIII

SUMMARY OF QUALITY EVALUATION OF FINISHED BACKS AND LEATHER YIELD ON WHITE WEIGHT BASIS

Tests No. 31 to 40, Inclusive

Test No.	Quality Evaluation of Backs					Quality Index	Leather Yield on White Weight %
	Color	Undertone	Finish	Temper	Drawn Grain		
31	100	87	100	97	85	94	64.2
32	100	96	88	100	98	96	65.9
32DN	100	98	88	100	99	97	66.7
33	96	80	92	100	81	90	60.7
34	97	94	86	100	95	94	65.9
35	98	91	88	100	94	94	66.0
36	100	95	88	100	98	96	65.2
37	100	91	83	100	89	93	65.6
37DN	100	100	90	100	91	96	66.0
38	100	97	91	100	96	97	66.8
39	100	97	83	100	99	96	62.3
40	100	88	86	100	95	94	61.7

the conclusions that leather quite comparable to conventional sole leather can be produced with the use of dialdehyde starch as the pretanning agent. However, it did show, to a degree, slightly more open grain, and there was a tendency of the dialdehyde starch leather to be slightly less firm than conventional sole leather. These conclusions also held true on the bellies produced.

The evaluation was also carried out on outsoles cut from the backs. Five backs from each of the matched-side tests (32, 32N, 37, and 37N) were cut into outsoles, graded, sorted, and rated at prevailing selling prices for the respective grades and selections. The results show that on this basis of evaluation the value of the soles cut from the dialdehyde starch–tanned backs was a stand-off with those cut from the control backs.

The dialdehyde starch bellies were also evaluated for insoles and counters at shoe factories, and the reports indicated that the insoles cut from these bellies channeled satisfactorily and that no difficulty was encountered in molding this leather into counters. The reports did comment however, on the lesser degree of solidity. Double shoulders were evaluated for waist belt leather and for welting. In both cases satisfactory handling of the dialdehyde starch leather was reported. The welting manufacturer did comment that the shoulders were slightly less firm than conventional leather used for welting.

In order to establish the cost of producing leather by this process an accurate account of all the materials used in the pretanning and retanning operations of these final 10 tests was maintained. Miles Chemical Company, one of the producers of dialdehyde starch, has stated publicly that the selling price of dialdehyde starch would be in the range of 30 to 40 cents per pound when large-scale commercial production is achieved. The material consumption data are shown in Table IX; they are based on the 3900 pounds of

TABLE IX

MATERIAL CONSUMPTION

Tests No. 31 to 40, Inclusive
100 Hides—3900 lb. Finished Leather

Operation	Material	Total lb.	lb./lb. Finished Leather
DAS pretan	DAS	195	0.050
	Sodium sulfate	517	0.132
	Sodium carbonate	20	0.005
Vegetable retan	Tannin*	1128	0.290

*Calculated from the rocker, tempering, and rinse liquors, and extract analyses.

finished leather produced from the 100 hides used in the final 10 tests. By applying the 30 cents per pound figure for dialdehyde starch and current published prices for sodium sulfate and sodium carbonate it is calculated that the material cost of the pretanning operation would be less than 2 cents per pound of leather produced. To this, of course, needs to be added the cost of the vegetable tannin used in the retanning operation. The amount of vegetable tannin used during this 10-test run was calculated from the

tan liquor analyses, and the figure obtained of .29 pound of tannin per pound of leather produced is believed to be below the industry average for producing sole leather by the straight vegetable tan process. The cost of the vegetable tannin will vary with the composition of the blend as well as market conditions. Based on the current prices of vegetable tanning materials and using the blend of extracts which is representative of that used by producers of sole leather, it is indicated that the reduced amount of tannin required when dialdehyde starch is used as the pretanning agent will permit the production of sole leather at a cost comparable to that of the sole leather industry today. Until such time as the dialdehyde starch is produced in quantities to permit the 30 to 40 cent per pound selling price this, of course, will not hold true. The use of dialdehyde starch as the pretanning agent will also permit a reduction in the time required to tan sole leather. Under the conditions of the final 10 tests carried out in this pilot plant study the tanning time from beam to the bleach was 13 days, which is appreciably below the industry average for tanning sole leather by the straight vegetable tanning process.

CONCLUSIONS

From the results of the numerous process and operational variables studied in the course of this pilot plant work, the following over-all conclusions appear to be warranted. Adequate deliming can be obtained with boric acid as the deliming agent. This eliminates the water wash required when ammonium salts are used. Satisfactory pretanning is obtained with the use of 5% dialdehyde starch on the white weight at a pH 8.0 for 48 hours in the rocker. The dialdehyde starch liquor can be reused at least 9 times by restrengthening with 3% dialdehyde starch. A stock solution of 25% dialdehyde starch dissolved with borax and having a pH of approximately 5 is stable for at least one month. A practical method for controlling the sodium sulfate content of the dialdehyde starch liquor based on specific gravity (barkometer) measurements has been developed.

Vegetable retan liquors made up from a conventional blend of tanning extracts to contain approximately 15% tannin in the pH range of 4 to 4.5 gave the best results under the conditions studied. The vegetable retan liquor can be reused with proper fortifications. There was no significant drop in the purity of this liquor, which indicates that there was no carry-over of impurities with the dialdehyde starch–pretanned hides and that there was no preferential uptake of the tannin from the liquor. To obtain complete vegetable retanning the wheel extracting and tempering operations are necessary.

The process can be adapted to existing sole leather operations with minor equipment changes. It is estimated that no more labor would be required than presently used in producing vegetable-tanned sole leather by the rocker tanning process. Tanning was completed from the beamhouse to the bleach

in 13 working days. This would permit some savings in inventory, and the tanner could work closer to the hide market.

A material balance study indicated that the amount of vegetable tannins required to obtain complete retannage was 0.29 pound per pound of finished leather. This is believed to be less tannin than required by the industry for straight vegetable-tanned sole leather. It is calculated that a price of approximately 30 to 40 cents a pound for dialdehyde starch would make the cost of the tannage comparable to present production.

The quality of the leather approaches conventionally tanned sole leather in all respects, except that the grain is slightly more open and the leather somewhat mellower. This is considered to be a matter of degree. The yield of leather is comparable to regular production. The results of the chemical and physical tests are essentially the same as those obtained on conventional sole leather.

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